

## THE CHEMISTRY OF SULFUR IN COAL—A HISTORICAL PERSPECTIVE

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### Introduction

Coal represents 85–90% of the fossil energy resources in the United States, and a quarter of the world's coal resources (1). Yet the full utilization of these resources has been limited by the presence of high levels of sulfur in many of the major deposits. (Fig. 1) This has been a recognized problem for many years. In the early part of the century, high sulfur content made use of some coals unsuitable for making of coke for metallurgical purposes. In recent years, the high sulfur content of coal has been recognized as the source of air pollution problems (acid rain), particularly from electricity generation and in industrial boilers. The Clean Air Act Amendments of 1990 were enacted to mitigate these problems. Earlier legislation restricted allowable SO<sub>2</sub> emissions in new power plants. The 1990 act however requires phased in limitation of SO<sub>2</sub> emissions in all power plants of over 25 MW capacity beginning in 1995, and is projected to reduce annual SO<sub>2</sub> emissions by about 10 million tons by the year 2000. A wide variety of methods of limiting SO<sub>2</sub> in flue gas have been devised from wet and dry limestone scrubbers, hot scrubbers, fluidized bed combustors, limestone injection into burners or ducts and others. Many of these are being developed and tested on a commercial scale under the Clean Coal Initiative. Under the 1990 Clean Air Act utilization of high sulfur coal without scrubbers or other remedial measures will not be permitted, although credits for lower than permitted levels may be used to compensate for emissions over permitted levels. This legislation will be expensive in new investment and operating costs and consumers are going to feel it.

### The Origin of Sulfur in Coal

Much of the sulfur in low sulfur coal derives from the sulfur content of the plant material making up the original peat. Sulfur contents greater than a few tenths of a percent have long been known to derive from the depositional environment. Sea water or brackish water in the coal beds contain sulfates. The sulfates undergo bacterial reduction to H<sub>2</sub>S which reacts with iron in the water to form pyrite and with the organic material or the sulfate reducing bacteria to form the organic sulfur structures. The reactions involved are not understood, but isotopic sulfur ratios support this conclusion (2,3).

### Sulfur in the Mineral Matter in Coal

It is well known that high sulfur coal usually contains both mineral sulfur which is largely pyrite, but can also include other metal sulfides and sulfates, and in some cases small amounts of elemental sulfur. It also contains sulfur in organic structures of a variety of types. (Table 1) There are well established methods for removal of much of the mineral sulfur compounds, based on density or wettability or other characteristics of the mineral.

Stock (4) and Buchanan (5,6,7) have shown that elemental sulfur is not present in pristene coal, but derives by oxidation of pyrite primarily. In any event, it is generally present in relatively small amounts even in oxidized coals.

### The Organic Sulfur Structures in Coal

Removal of the organic sulfur is much more difficult than the pyritic sulfur, as it is part of the organic coal structure itself. Processes have been developed for removal of both organic and inorganic sulfur involving molten caustic at high temperatures (e.g., the TRW Gravimelt Process) or oxidizing agents such as air, or chlorine in the presence of strong alkali (e.g., the Ames, PETC and Ledgemont oxydesulfurization Processes). (8) None of these appear to be economically practical at the present time. All of them have been developed without any real knowledge of the chemistry of the organic sulfur they

are supposed to remove. In the Second Supplementary Volume of the "Chemistry of Coal Utilization" which came out in 1981 it says:

"Since there are few methods for determining the functionality of sulfur, especially in mixtures, and the few that are available either are ambiguous or give questionable results with coal, the nature and bonding of the organic sulfur in coal is still unknown."

Since that was written, much progress has been made by many researchers including our Storch Awardee and his coworkers. I am therefore going to devote the limited time I have to outline some of the scientific advances that have been made toward understanding the chemistry of the organic sulfur components, and the status of our knowledge of the organic sulfur structures in coal, as I perceive it today. This progress has been the result of development of a number of new analytical techniques that have become available and considerable research ingenuity by a number of coal scientists.

The organic sulfur in coal can vary from a few tenths of a percent to several percent. Usually, the pyritic sulfur content is similar to the organic sulfur content. In some rare coals however, the pyritic sulfur is very low and the organic sulfur very high. That is the case for two coals from Spain and Yugoslavia (see table 2) which have been the subject of considerable study by coal scientists because they allow the study of the organic sulfur with little interference from the pyrite (46,47,48). Similar coals exist from India and New Zealand.

It has been known for many years, that coal produces thiophenic compounds as tars upon coking, pyrolysis or in coal hydrogenation. That these heterocycles are actually part of the coal structure and not formed in the processing was demonstrated by Hayatsu (9,10) with sodium dichromate oxidation of a range of coal ranks from lignite to anthracite and converting the resulting acids to the methyl esters. Of some 141 aromatic structures obtained in this work were thiophene, benzothiophene, dibenzothiophene and a number of methyl substituted compounds of those same heterocycles. Since that time, Nishioka et al. (11, 12), Curt White (13,14), Sinnighe Damste and de Leeuw (15, 16) and a number of other workers have identified other heterocyclic structures either produced by solvent extraction, pyrolysis or coal hydrogenation. The development of Flame Photometric Detectors (FPDS) was important in some of this work. Winans and Neill (17) also found a number of multiple- heteroatom-containing sulfur compounds where there was oxygen or nitrogen or both in addition to the sulfur by flash pyrolysis of coal into a high resolution mass spectrometer (fig. 2). There can be little doubt that there are sulfur heteroatoms in the aromatic clusters of most high sulfur coals. But is that the only form of sulfur in the organic portion of coal?

When Pittsburgh 8 coal which contained about 1.5% organic sulfur was pyrolyzed by a pyroprobe into a high resolution mass spectrometer many sulfur containing products including low molecular weight compounds such as  $H_2S$ , COS,  $CH_3SH$ ,  $SO_2$ , and  $CS_2$  as well as a whole range of heterocyclic structures from thiophene, benzothiophene, dibenzothiophene and many alkyl substituents of these heterocycles were detected. (18) When the same coal had over 90% of the mineral matter removed by a non-chemical process so as not to affect the organic structures present, a very similar set of pyrolysis products were produced with only the  $SO_2$  and  $CS_2$  largely eliminated. (Table 3) With the mineral sulfur compounds removed from the system, this suggests that the low molecular weight sulfur compounds are produced by breakdown of some relatively unstable organic sulfur structures in the coal, while the more stable heterocyclic sulfur structures pyrolyze into the mass spectrometer unchanged. What are these unstable sulfur structures?

Coal of course is a very heterogeneous material, consisting not only of mineral matter as I have already mentioned, but also quite distinct macerals, deriving from different components of the plant material which went into forming the coal. Raymond of Los Alamos (19,20) studied the organic sulfur content of the various macerals, without separation, from 8 different coals by electron probe microanalysis and showed that the sulfur content is not the same in the various macerals of a given coal. Wert et al. at the University of Illinois (21) made similar measurements on Illinois #5 coal by Transmission Electron Microscopy and showed that the sporinite contained twice as much sulfur as the vitrinite (Fig. 3). Purified

macerals prepared by Dyrkacz' (22) method for separating the various macerals from coal by Density Gradient Centrifugation have been shown by Dyrkacz and Wert (23) and Hippo and Crelling (24) to also have different organic sulfur contents in the various macerals of the same coal.

"Pure" macerals, we must remember still consist of mixtures of macromolecules having a rather random distribution of component molecules. In most cases these are cross-linked and insoluble and therefore intractable. Most researchers in the field therefore resort to trying to identify the various sulfur functional groups or substituents in coal without regard to the rest of the coal structure, since they are the components whose chemistry we want to identify and presumably remove.

In the late 1970s Attar and his coworkers (25,26,27) developed an interesting approach to determining the sulfur functional groups in coal by catalytic programmed temperature reduction to  $H_2S$ . He obtained "kinetograms" (fig. 4) which showed peaks of  $H_2S$  production at various temperatures which from model compound experiments he identified with the various sulfur functional groups which were present. This approach had the problem of requiring adequate contact of a solid catalyst with a solid coal, and recoveries of the sulfur were often low. However he did obtain discrete peaks which he associated with such functional groups as thiolic (mercaptan), thiophenolic, aliphatic sulfide, aryl sulfide, thiophenic and pyrite.

LaCount and coworkers (28,29) came up with a similar approach based on the programmed temperature oxidation of coal in which the sulfur components were oxidized to  $SO_2$  which was detected by FTIR.  $SO_2$  evolution peaks were obtained at various temperatures which were again related to specific sulfur functional groups by comparison with model polymeric sulfur compounds. Peaks were identified with pyrite, non-aromatic sulfur and aromatic sulfur, which presumably includes thiophenic sulfur. In a recent paper, LaCount showed the presence of significant amounts of non-aromatic sulfur groups which he found to be a larger proportion of the total organic sulfur in the low rank coals than in the higher rank coals.

Similar results were obtained in isothermal flash pyrolysis experiments (18). If model sulfur compounds are pyrolyzed at various temperatures at fast heat up rates and very short contact times, to avoid secondary reactions, a set of curves such as those shown in figure 5 are obtained. The aliphatic mercaptans, sulfides and disulfides break down to form  $H_2S$  at a much lower temperature than the aromatic sulfides and thiophenic compounds. When similar isothermal pyrolysis experiments are applied to coals, significant amounts of  $H_2S$  are produced at temperatures in the range where the aliphatic sulfur groups are unstable. The proportion of organic sulfur groups of the thermally unstable types are found to be higher in the low rank coals, and decrease as the rank increases. This suggests that coalification either converts the unstable sulfur structures of the coal to thiophenic structures, or destroys them leaving the thiophenic sulfur structures intact.

It would of course be desirable to have an analytical method for the various sulfur functional groups without the danger of thermally converting the sulfur compounds to other sulfur structures. In the process, as could be the case with the three methods I have described. At least two laboratories undertook to do this with X-ray methods. Gorbaty and coworkers at EXXON used Sulfur K edge X-ray absorption near edge structure spectroscopy (XANES) and X-ray Photoelectron spectroscopy (XPS) (30,31), and Huffman and coworkers at the University of Kentucky also used XANES (32,33). The EXXON group found it necessary to use a third derivative analysis of the XANES spectra to get a resolution of the aliphatic, aromatic and pyritic sulfur forms, while with the XPS they were able to deconvolute the original spectra into identifiable sulfur components. Table 4 shows the breakdown of sulfur types they obtained on the 8 Argonne premium coal samples. The Kentucky group after initially being unable to see the aliphatic structures were able to deconvolute the XANES spectra into component sulfur types at which time the presence of the aliphatic sulfur components became apparent (fig. 6). Suffice it to say that both aliphatic and aromatic or heterocyclic sulfur structures are resolvable in the various coals, and the previously observed trend of higher aliphatic sulfur in the low rank coals decreasing in the higher rank coals is also apparent.

Comparison of analysis of sulfur type on the same low pyrite-high organic sulfur coals by flash pyrolysis and X-ray methods shows quite a reasonable agreement concerning the content of the more reactive aliphatic sulfur components. (34) (Table 5) The higher aliphatic value for the Rasa coal by pyrolysis than by X-ray apparently is due to the presence of some aromatic disulfide which was shown to be less stable than other aromatic sulfides. Combined pyrolysis and X-ray studies also provided evidence that aliphatic sulfidic sulfur is thermally converted to aromatic or heterocyclic sulfur forms, supporting the view that coalification results at least in part in conversion of aliphatic to aromatic and heterocyclic sulfur. (35)

Recently, Brown of CANMET and coworkers (36,37) have introduced another X-ray method based on the sulfur L edge X-ray absorption near-edge spectra. This method offers the potential of greater resolution than the K edge analysis. It has the disadvantage of requiring high vacuum, (the K edge method can be run at atmospheric pressure) thereby limiting the range of samples that can be run. However the greater resolution makes further investigation of this technique worthwhile.

While unoxidized (pristine) coals clearly contain sulfur in the reduced state, the X-ray techniques can also distinguish among the oxidized forms of sulfur such as sulfoxides, sulfones, sulfonic acids and sulfate. This was utilized by both the EXXON (38) and U. of Kentucky groups (39) to show that the aliphatic sulfides are selectively oxidized to sulfoxides and sulfones, and in some cases sulfonic acids, if disulfides are present.

Hippo and the group at Southern Illinois University (40) have done oxidation studies on coals and coal macerals derived from them, using peroxyacetic acid which solubilized most of the coals. The oxidation products were methylated with diazomethane and analyzed in a gas chromatograph using a flame photometric detector. Ten or twelve sulfur compounds were detected, with methyl sulfonic acid being a major product, presumably derived from aliphatic disulfides or thiophene.

The existence of organic sulfur in coal as both aliphatic and aromatic or heterocyclic sulfur forms was dramatically demonstrated by Stock and coworkers together with the EXXON group. They showed that single electron transfer reagents such as potassium naphthalenide in tetrahydrofuran will attack and destroy heterocyclic sulfur compounds and not the aliphatic or sulfidic sulfur. (41) They also showed that strong organic bases such as *n*-butyl lithium and potassium *t*-butoxide in heptane remove the sulfidic sulfur from model compounds without affecting the thiophenic compounds. (42) They performed these treatments individually on Illinois #6 coal from which the pyrite had been removed, and showed that the organic sulfur type corresponding to the particular method of treatment was removed as shown by the XANES method. Also, stepwise treatment of the same coal with each reagent eliminated both sulfidic and heterocyclic sulfur types from the coal. (43)

As I have discussed, we now have considerable evidence that the sulfur in coal exists as both aliphatic and aromatic or heterocyclic forms, and several methods exist for the approximation of the amounts of each. Low rank coals contain more of the organic sulfur in aliphatic or labile forms, whereas higher rank coals contain predominantly heterocyclic sulfur. Reaction of coals with methyl iodide (18) suggests that at least some of the aliphatic sulfur is present as thioether, and some possibly as disulfides. Very little appears to be present as mercaptan.

#### **Sulfur Removal from Coal**

What are the implications of this information for the development of an effective high yield low cost process for sulfur removal from coal? Since there are at least two distinct organic sulfur forms, any process devised for such removal must take this into account. Palmer and Hippo et al. (44) found that a combination of peroxyacetic acid treatment and either thermal or base treatment removed much of the organic sulfur. Stock's two processes appear to be unlikely to be practical on a commercial scale, but may lead to similar lower cost methods. With the lower rank coals containing a larger percentage of the less stable aliphatic sulfur, removal of that portion of the organic sulfur together with the pyritic sulfur with strong alkali may be sufficient for most purposes. There is also a number of research programs

underway investigating bacteriological methods for sulfur removal (45). These might be expected to be slow but low in cost if the proper organisms are found.

### Summary and Conclusions

- 1) At least two classes of organic sulfur structures appear to be present in coals, with the low rank coals generally containing a larger percentage of the total sulfur as more reactive aliphatic sulfur components. As rank increases, the more stable heterocyclic sulfur structures increase and become predominant.
- 2) Analytical methods exist for approximating the amount of the two component classes, although more precise methods are needed.
- 3) We now have the fundamental basis and analytical methods for further development of processes for removal of organic sulfur from coal. Such processes must recognize the presence of the two types of sulfur structures.
- 4) We still do not understand the reactions occurring between  $H_2S$  and the biomass that formed the organic sulfur structures in the first place.
- 5) We also do not understand the reactions of  $H_2S$  and/or elemental sulfur with coal or char at elevated temperatures as has often been observed.

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Table 1. Sulfur Content Of Some United States Coals (Wt. %)

Type of Sulfur	Texas Lignite Martin Lake	Wyodak Subbit.	Ill #6	Hi Vol Bit. Ohio #6
Pyritic	0. 14	0. 11	1. 06	1. 15
Sulfate	0. 03	0. 12	0. 12	0. 03
Organic	1. 05	0. 70	2. 17	2. 01
Total	1. 22	0. 93	3. 35	3. 19

Table 2. Total and Organic Sulfur Contents of Two High-Sulfur Low-Pyrite Coals

Coal	Country of Origin	% Carbon (maf basis)	% Total Sulfur	% Organic Sulfur
Mequinenza	Spain	68. 6	12. 6	11. 8
Rasa	Yugoslavia	80. 2	11. 8	11. 4

Table 3. Pyroprobe GC/MS Analysis of Pittsburgh 8 R &amp; F High Sulfur Coal

Product	% Tot. Area	
	raw	90% of Pyrite Removed
H <sub>2</sub> S	3. 03	4. 83
COS	0. 48	0. 31
CH <sub>3</sub> SH	0. 32	0. 34
SO <sub>2</sub>	2. 13	0. 02
CS <sub>2</sub>	0. 27	0. 06
thiophene	0. 25	0. 22
methylthiophene-1	0. 34	0. 23
methylthiophene-2	0. 23	0. 10
dimethylthiophene-1	0. 49	0. 46
dimethylthiophene-2	0. 47	0. 38
dimethylthiophene-3	0. 38	0. 24
dimethylthiophene-4	0. 07	0. 05
trimethylthiophene-1	0. 19	0. 10
trimethylthiophene-2	0. 22	0. 16
tetramethylthiophene	low	0. 04
benzothiophene	0. 29	0. 24
methylbenzothiophene-1	0. 06	0. 04
methylbenzothiophene-2	0. 13	0. 15
methylbenzothiophene-3	0. 20	0. 19
methylbenzothiophene-4	0. 15	0. 14
methylbenzothiophene-5	0. 17	0. 12
methylbenzothiophene-6	—	0. 02
Dimethylbenzothiophene-1	0. 11	0. 11
dimethylbenzothiophene-2	0. 06	0. 05
dimethylbenzothiophene-3	0. 12	0. 14
dimethylbenzothiophene-4	0. 07	0. 10
dimethylbenzothiophene-5	0. 05	0. 04
dimethylbenzothiophene-6	0. 07	0. 08
dimethylbenzothiophene-7	0. 05	0. 04
dimethylbenzothiophene-8	0. 05	0. 03
dimethylbenzothiophene-9	0. 03	0. 02
dibenzothiophene	0. 08	+

Calkins, W. H. (18)

Table 4. Approximate Quantification of Organically Bound Sulfur Forms in Argonne Premium Coal Samples

Coal	%C dmmf	Mole percent (+10) by XANES		
		aliphatic	aromatic	thiophenic
Beulah-Zap	74. 05	35	25	38
Wyodak-Anderson	76. 04	33	22	45
Illinois #6	80. 73	33	26	41
Blind Canyon	81. 32	24	28	47
Pittsburgh 8	84. 95	22	34	44
Lewiston-Stockton	85. 08	19	20	60
Upper Freeport	88. 08	13	30	57
Pocahontas #3	91. 81	13	23	64

G. N. George, M. L. Gorbaty, S.R. Kelemen and M. Sansone (30)

Table 5. Percent of Organic Sulfur as Aliphatic Sulfur by Pyrolysis and X-ray Methods

coal	country of origin	% carbon (maf basis)	% total S	% organic S	by pyrolysis	% aliphatic sulfur		mol % H <sub>2</sub> S by TPD
						by X-ray		
						XANES	XPS	
Mequinenza	Spain	68.6	12.6	11.8	67	48	66	75
Beulah-Zap	USA	72.9	0.88	0.70	39	37	45	
Wyodak-Anderson	USA	75.0	0.63	0.47	36	33	37	
Charming Creek	NZ	78.7	5.85	5.76	26	28	38	29
Rasa	Yugoslavia	80.2	11.8	11.4	47	30	26	40

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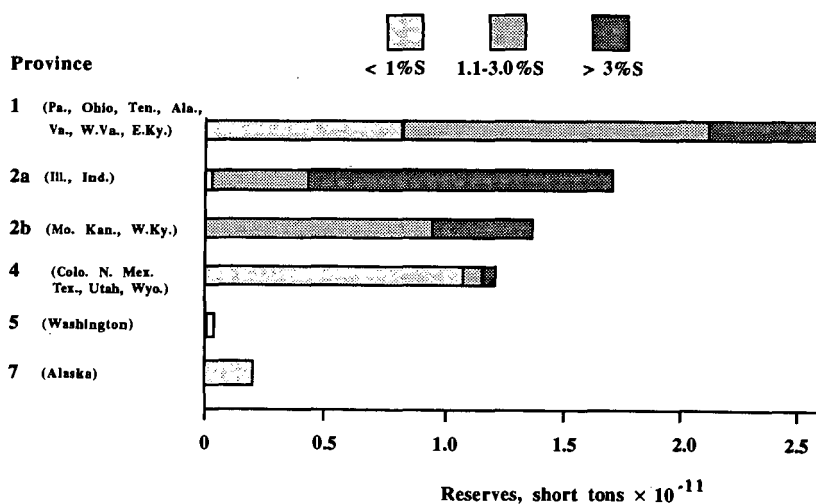


Figure 1. Distribution of U.S. bituminous coals by geological province and sulfur content.



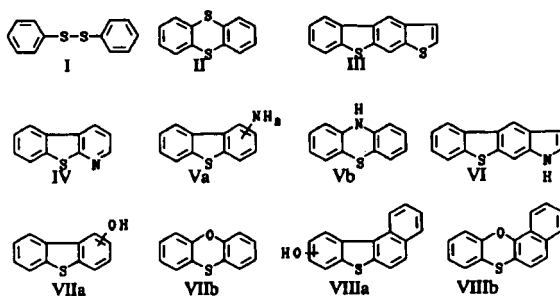


Figure 2. Possible Multiple-heteroatom-containing pyrolysis products. [R. E. Winans and P. H. Neill (17)]

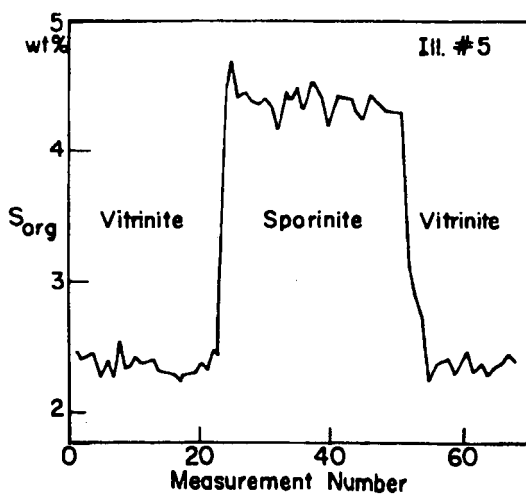


Figure 3. Change in organic sulfur concentration for a maceral of sporinite embedded in a maceral of vitrinite, Illinois #5 Coal. [C. Wert, Y. Ge, B. H. Tseng, and K. C. Hsieh (21).]

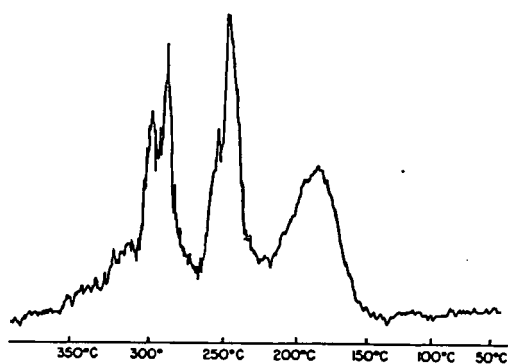


Figure 4. Reductive Kinetogram of Illinois #6 Coal. [A. Attar and F. Dupuis (25).]

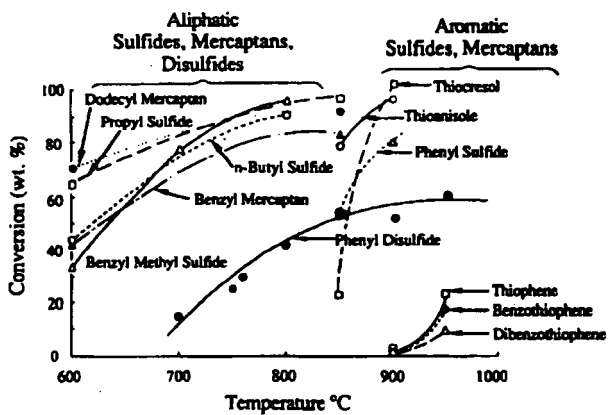


Figure 5. Pyrolysis of Model Sulfur Compounds (% Conversion vs. Temperature) 0.5 sec. Contact time. W. H. Calkins (18)

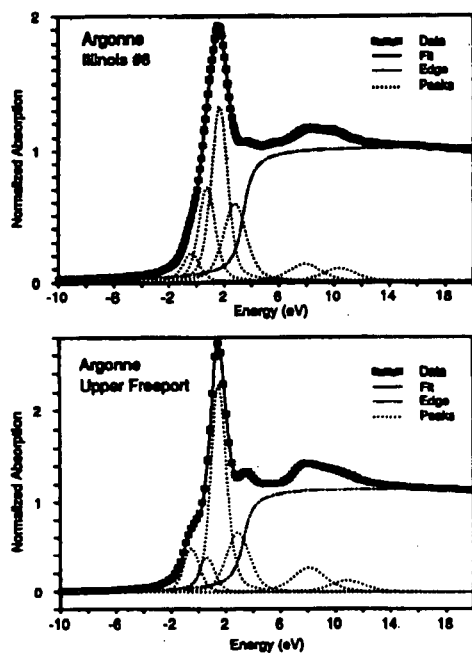


Figure 6. Least Squares Fits of the XANES of Illinois #6 and Upper Freeport Coals. [G. P. Huffman, S. Mitra, F. E. Huggins, N. Shah, S. Vaidya, and F. Lu (33).]